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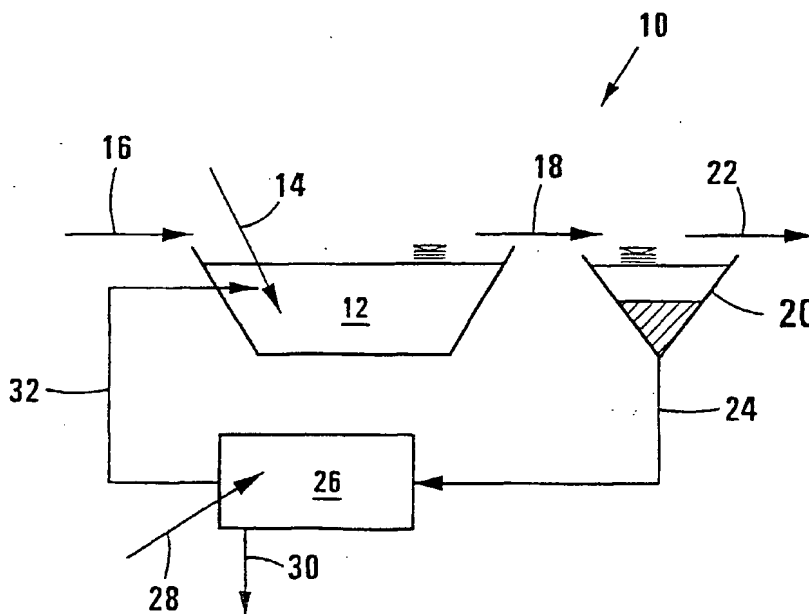
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(54) Title: TREATMENT OF METAL CONTAINING WATER BY THE ADDITION OF MAGNETITE



(57) Abstract: A process for treating water includes adding magnetite seed to water containing dissolved ferrous and/or non-ferrous metals, to form seeded water. If necessary, ferrous iron is added to the water, and the pH of the seeded water is raised to a level at which a solid ferrous intermediate forms, or is present, in the seeded water and/or the water is maintained at such a pH level. The resultant seeded ferrous intermediate-containing water is subjected to controlled oxidation of the ferrous intermediate at substantially ambient temperature to produce, as an oxidation product, ferrite(s) comprising magnetite. At least a predetermined or threshold ferrous intermediate concentration is maintained in the water during the controlled oxidation of the water. Ferrite is separated from the water.

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TREATMENT OF METAL CONTAINING WATER BY THE ADDITION OF MAGNETITE

THIS INVENTION relates to the treatment of water. It relates in particular to a process for treating water, particularly acid mine drainage water or industrial wastewater, to remove dissolved ferrous and/or non-ferrous metals from the water.

According to the invention, there is provided a process for treating water, which includes

- adding magnetite seed to water containing dissolved ferrous and/or non-ferrous metals, to form seeded water;

- if necessary, adding ferrous iron to the water;

- if necessary, raising the pH of the seeded water to a level at which a solid ferrous intermediate forms, or is present, in the seeded water and/or maintaining the water at such a pH level;

- subjecting the resultant seeded ferrous intermediate-containing water to controlled oxidation of the ferrous intermediate at substantially ambient temperature to produce, as an oxidation product, ferrite comprising magnetite;

- maintaining at least a predetermined or threshold ferrous intermediate concentration in the water during the controlled oxidation of the water; and

- separating the ferrite from the water.

In addition to containing dissolved ferrous iron, the water may also contain dissolved non-ferrous metals such as heavy metals. The water may even, initially, contain only dissolved non-ferrous metals and little or no ferrous iron. The process may thus include adding ferrous iron to the water, preferably before or simultaneously with the addition of the magnetite seed. The water may thus, in particular, be a raw wastewater such as acid mine drainage (AMD) or an industrial wastewater.

The pH to which the seeded water is raised and/or is maintained, is thus such that the solid ferrous intermediate forms, or is present, in the seeded water. The Applicants have found that when the pH of the seeded water is greater than about 6, ferrous iron exists in the solid phase, and is therefore called ferrous intermediate. The pH to which the seeded water is raised and/or at which it is maintained, may be at least 9.0, typically about 10.5. The raising of the pH of the water and/or the maintenance of the pH thereof, may be effected by adding a hydroxide or lime to the water. The Applicants have found that the water pH affects the end product i.e. the ferrite and magnetite that are formed.

The controlled oxidation may be effected in an oxidation reactor, and may be effected by aerating the seeded ferrous intermediate-containing water. The rate of oxidation of ferrous intermediate depends on the rate of dissolved oxygen supply. For a given oxidation reactor design operating under given conditions, the rate of dissolved oxygen supply depends on the air flow rate, i.e. the rate of aeration.

The rate at which the seeded ferrous intermediate-containing water is aerated may be controlled or adjusted so that the rate of oxidation of ferrous intermediate is compatible with the formation of ferrite(s) consisting mainly of magnetite. If the rate of ferrous intermediate oxidation is too high, non-ferrite and non-magnetite end-products will be formed. In other words, the rate of aeration is controlled so that the ferrous intermediate oxidizes primarily to ferrite(s) consisting mainly of magnetite, with substantially no non-ferrite compounds forming.

Where the ferrite so-produced is magnetite, this magnetite may be partially oxidised. Partially oxidized magnetite has a lower molar percentage ferrous component than stoichiometric magnetite in which the molar percentage ferrous component is 33.33%. The degree to which the magnetite is oxidised is dependant on the magnetite seed concentration and on the rate of oxidation of ferrous intermediate.

Sufficient magnetite seed may be added to the ferrous-containing water so that the molar ratio of the initial seed (as Fe): ferrous intermediate (as Fe) is at least 1:1.

The Applicant has also found that the water temperature affects the end product, i.e. the ferrite/magnetite. Thus, the ambient temperature at which the seeded water is subjected to the controlled oxidation, may be from 5°C to 25°C or higher.

The process may be operated in either a batch manner or in a steady state continuous manner, i.e. steady state as regards the seed and ferrous intermediate concentrations.

When the process operates in a steady state continuous manner, it may include a contact-separation sequence in which raw water containing dissolved ferrous and/or non-ferrous metals is mixed with water containing magnetite seed and ferrous intermediate at an elevated pH of at least 9.0, and typically around 10.5, whereafter solid components present in the resultant water mixture are partially separated from the water phase i.e. some water remains with the solids so that they are in the form of a sludge, slurry or suspension, with the solid components in the fraction of water in which they are suspended, i.e. the sludge, slurry or suspension, then being subjected to the controlled oxidation.

This contact-separation sequence has at least four important effects or consequences. Firstly, it serves to concentrate the seed and any precipitated components, including ferrous intermediate, prior to subjecting the seeded water to the controlled oxidation. The quantitative increase in the concentration of the seed and any precipitated components including ferrous intermediate, will consequently be according to the concentrating factor, i.e. the ratio between the total volume and the volume occupied by the now concentrated solid components. If oxidation is withheld, the ferrous intermediate concentration may be increased to any desired value by virtue of the contact-separation sequence concentrating step.

Secondly, the contact-separation sequence has the effect of separating all precipitated components, including all ferrous and non-ferrous metals present in the raw water, from the bulk volume of the raw water, prior to oxidation. In this way, the precipitation reaction, which may take place in a contact reactor, is uncoupled from the oxidation-mineral formation reaction which occurs in the oxidation reaction and is the rate-limiting step. Consequently, the flow rate of the bulk volume of the wastewater in

the system is uncoupled from the rate-limiting step, resulting in a vastly reduced hydraulic retention time for this (potentially massive volume of) water. This uncoupling also allows for a smaller oxidation reactor than would otherwise be necessary. The relative reduction in the volume of the oxidation reactor will be in proportion to the same concentrating factor mentioned above. The uncoupling of the flow rate of the bulk volume of the wastewater in the system from the rate-limiting step is a unique feature distinguishing this process from HDS-type AMD treatment processes.

Thirdly, the contact-separation sequence has the effect of increasing the concentration of the seed and all precipitated components including all ferrous and non-ferrous metals, relative to any dissolved components in the water. This increase in concentration will be in proportion to the same concentrating factor mentioned above.

Since the precipitation reaction is so rapid, the rate-limiting step with respect to the hydraulic retention time of the bulk wastewater flow is the separation step. Both the rate of separation and the concentrating effect of the contact-separation sequence may depend upon the ferrite/magnetite seed concentration and upon the seed : ferrous intermediate ratio. Achieving a rapid separation rate and suitable concentrating factor may therefore be a factor which determines the ferrite/magnetite seed concentration and the seed : ferrous intermediate ratio.

Fourthly, the contact-separation sequence allows the possibility of separating precipitated metals as metal intermediates (analogous to and including ferrous intermediate) from the bulk flow; but instead of proceeding to ferrite formation via oxidation, recovering the precipitated metals by remobilization into the aqueous phase, thereby regenerating the seed for recycling.

The ferrous intermediate concentration in the water is thus maintained at the predetermined or threshold value, or at a higher value. The ferrous intermediate concentration in the water may be controlled or adjusted so that the oxidation of the ferrous intermediate, during the controlled oxidation, is compatible with the formation of ferrite(s) consisting mainly of magnetite. If the ferrous intermediate concentration is too low, i.e. below the predetermined or threshold value, non-ferrite and non-magnetite end-products will be formed. In other words, the ferrous intermediate concentration in the

water is controlled so that the ferrous intermediate, during the controlled oxidation, oxidizes primarily to ferrite(s) consisting mainly of magnetite, with substantially no non-ferrite compounds forming. When the process is a steady state continuous process, the predetermined or threshold ferrous intermediate concentration in the water may be about 500mg/ℓ.

The maximum rate of ferrous intermediate oxidation which will result in the formation of ferrite/magnetite end-products, without resulting in the formation of other iron oxide end-products, is in proportion to the steady state ferrous intermediate concentration. In other words, the higher the steady state ferrous intermediate concentration, the higher is the allowable rate of ferrous intermediate oxidation which will avoid non-ferrite/non-magnetite formation.

The process may include, when the ferrous-containing water contains also calcium, and when the process is a steady state continuous process operating in the manner hereinbefore described, maintaining the magnetite seed concentration at a higher level than when the ferrous-containing water does not contain calcium, in order to counter the inhibitory effect which calcium has on ferrite and magnetite formation.

Calcium is typically present in the ferrous-containing water when lime is used to increase the pH of the water. In the presence of calcium, large amounts of undesired non-ferrite/magnetite iron oxides are formed; it is thus, to counter the formation of these non-magnetic iron oxides, that the seed concentration is then increased.

When the process is a steady state continuous process and calcium is present in the water, the process will thus also include maintaining at least a predetermined or threshold ferrous intermediate concentration during the controlled oxidation, as hereinbefore described. Where calcium is present, the predetermined or threshold ferrous intermediate concentration required to ensure the formation of ferrite/magnetite end-products, will typically be higher than that required when calcium is not present. Thus, the predetermined or threshold ferrous intermediate concentration in the water, when the water contains calcium, may be about 1200mg/ℓ. However, when the seeded ferrous intermediate containing water is saturated or even slightly supersaturated with dissolved calcium, the threshold ferrous intermediate concentration

required to prevent the formation of non-ferrite/magnetite end-products may be in the region of 1500mg/ℓ or higher. In general this may represent a ferrous intermediate (as Fe) : dissolved calcium (as Ca) molar ratio of around 5 : 1.

When calcium is present, maintaining the ferrous intermediate concentration above the threshold limit may be effected by concentrating the seed and any precipitated components including ferrous intermediate, prior to subjecting the seeded water to the controlled oxidation, i.e. employing a contact-separation sequence as hereinbefore described. Quantitatively, the increase in the concentration of the seed and any precipitated components including ferrous intermediate, will consequently be according to the concentrating factor, i.e. the ratio between the total volume and the volume occupied by the now concentrated solid components. If oxidation is withheld, the ferrous intermediate concentration may be increased to any desired value by virtue of the contact-separation sequence concentrating step.

When calcium is present, concentrating the seed and any precipitated components prior to subjecting the seeded water to the controlled oxidation, i.e. the contact-separation sequence, has the effect of increasing the ferrous intermediate (as Fe) : dissolved calcium (as Ca) molar ratio. Quantitatively, the increase in this ratio will be according to the concentrating factor, i.e. the ratio between the total volume and the volume occupied by the now concentrated solid components. However, if oxidation is withheld, the ferrous intermediate concentration, and therefore the ferrous intermediate (as Fe) : dissolved calcium (as Ca) molar ratio, may be increased to any desired value by way of the contact-separation sequence concentrating step.

When calcium is present, the contact-separation sequence has the further effect of separating all ferrous and non-ferrous metals present in the raw water, from the bulk volume of the raw water, prior to oxidation. This allows for a smaller oxidation reactor than would otherwise be necessary. The relative reduction in volume of the oxidation reactor will be in proportion to the same concentrating factor mentioned above.

When calcium is present, the concentrating effect of the contact-separation sequence may depend upon the ferrite/magnetite seed concentration. Achieving a

suitable concentrating factor may therefore be a factor which determines the ferrite/magnetite seed concentration.

When all of the above apply, the threshold ferrous intermediate concentration required in order to ensure the formation of ferrite end-products, may vary according to the type(s) and concentration(s) of non-ferrous ions present in the water. In some cases, depending upon the characteristics of the raw water and/or upon the desired characteristics of the end-products, it may not be necessary or desirable or possible to form end-products made up of only ferrites. In such cases, the threshold ferrous intermediate concentration and/or the ferrous intermediate (as Fe) : dissolved calcium (as Ca) ratio and/or any other parameter (e.g. rate of oxidation) may be set at a value in accordance with the prevailing conditions or desired or possible outcomes.

The separation may be effected in a gravity settler.

The inventors have thus, in the present invention, confirmed the feasibility of a one-step ambient temperature ferrite process. The use of seed, the maintenance of a threshold ferrous intermediate concentration; and where calcium is present, the maintenance of a higher threshold ferrous intermediate concentration, thus facilitates the formation of ferrite/magnetite by the air oxidation of waters containing dissolved ferrous iron and/or non-ferrous metals, such as AMD or industrial wastewaters, at ambient temperature.

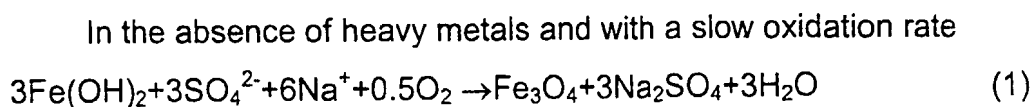
Acid mine drainage (AMD) impacts negatively on fresh water resources in the mining areas of South Africa and many other parts of the world. AMD waters are extremely variable but are frequently characterized by low pH, very high iron concentrations, significantly high concentrations of non-ferrous (mainly heavy) metals, and very high salinity, principally in the form of sulphates. The chemical make-up of AMD is directly explicable in terms of the biogeochemical process whereby AMD arises: put most simply, mining activities allow atmospheric oxygen and water to contact and, together with the action of aerobic bacteria, oxidize iron pyrite (FeS_2) in the rock. This releases sulphate and iron into underground water making the latter strongly acidic, causing leaching of non-ferrous metals from the rock, as described in Kleinmann RLP, Crerar DA and Pacelli RR (1981) Biogeochemistry of acid mine drainage and a method

to control acid formation. Mining Engineering, 300-305. A comprehensive solution to AMD pollution requires both metal and sulphate removal. The latter can be effected by either biological or membrane-based methods. Irrespective of the method of sulphate removal, iron and non-ferrous metals must be removed beforehand.

Current strategies for metal removal from AMD have several shortcomings, as described in Loewenthal RE, Morgan BE, and Lahav O, Iron and heavy metals in acid mine drainage waters - equilibrium and treatment considerations. Water, Sewage and Effluent (2001), 21(1), and Bosman DJ (1983) Lime treatment of acid mine water and associated solid/liquid separation, Wat. Sci. Tech., 15: 71-84. The high density sludge (HDS) process, deployed on several South African mines, utilizes lime for pH adjustment and oxygen to vigorously oxidize ferrous iron. A recycle loop is used to densify the precipitant which is otherwise difficult to separate from the liquid phase. High oxygen concentrations are required. These limitations, coupled with the magnitude of the AMD problem (some mining basins pump up to 60Mℓ of water per day), underscore the need for improved cost-effective treatment methods.

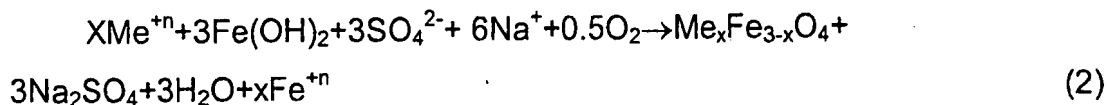
Magnetite is a partially oxidized iron oxide with the formula Fe_3O_4 (i.e. $\text{Fe}^{3+}_2\text{Fe}^{2+}\text{O}_4$). Thus, it conforms to the general formula $\text{M1}^{3+}_2\text{M2}^{2+}\text{O}_4$ for ferrites, where M1 and M2 stand for any of a number of possible metal elements. Magnetite is a ferrite in which the metal component is made up purely of iron. If a solution dominated by soluble iron but containing smaller concentrations of other divalent and trivalent metal species (such as are found in AMD) is transformed into ferrite, then the resulting precipitant will be dominated by magnetite but some of the iron atoms will be replaced by non-ferrous cations, making for 'substituted magnetite' or 'mixed-species' ferrites.

Barrado E, Prieto F, Vega M and Fernandez-Polanco F (1998) Optimization of the operational variables of a medium scale reactor for metal containing waste water purification by ferrite formation. Wat. Res. 32(10), 2055-2061 proposed the following stoichiometric reactions for ferrite formation from ferrous at $\text{pH} > 10.5$:



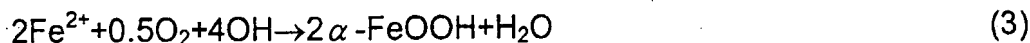
Equation (1) shows that alkalinity is neither produced nor consumed during the formation of magnetite from ferrous hydroxide, and that 10.47mg/ℓ of magnetite (as Fe) are formed for every 1mg/ℓ of oxygen consumed.

In the presence of heavy metals and with a slow oxidation rate



Fe^{+n} represents the total concentration of iron which is replaced by metal cations in the ferrite structure. This displaced iron will appear as ferrous or ferric depending on the valence of the displacing cation. These ferrous and ferric ions will react to form magnetite.

However, it is to be noted that with excess oxidizing agent, goethite is formed instead of magnetite:



The formation of relatively pure precipitates of magnetite from ferrous solutions was until recently thought to be possible only at temperatures greater than 90°C, as described in Kiyama M (1974) Conditions for the formation of Fe_3O_4 by the air oxidation of $Fe(OH)_2$ suspensions. Bulletin of the chemical society of Japan, 47(7), 1646-1650, and Cornell RM and Schwertmann U (1996) The iron oxides: structure, properties, reactions, occurrence and uses. VCH, Germany. Nevertheless, the capacity of magnetite to absorb by cation substitution non-ferrous metals, plus the advantageous settling properties of magnetite, have resulted in the exploitation of magnetite formation as a means to remove metal ions from waste streams. The 'ferrite process' refers to a high temperature process (65°C) developed in Japan for the treatment of laboratory wastes containing heavy metals, as described in Katsura T, Tamaura Y and Terada H (1977) Treatment of the laboratory wastewaters by the magnetic separation process, Indust Water 233: 16-21; Tamaura Y, Tu PQ, Rojarayanont S, and Abe H (1991a) Stabilization of hazardous materials into ferrites. Wat. Sci. Tech. 23: 399-404; and Tamaura Y, Katsura T, Rojarayanont S, and Abe H (1991b) Ferrite process: heavy

metal ion treatment system. Wat. Sci. Tech. 23: 1893-1909. However, during the last decade, several developments in the field of ambient temperature ferrite chemistry have occurred which appear to be opening the way to treating large volumes of water such as AMD.

Tamura Y, Katsura T, Rojarayanont S, and Abe H (1991b) Ferrite process: heavy metal ion treatment system. Wat. Sci. Tech. 23: 1893-1909 first applied the ferrite process at ambient temperature as a two-step process in which a ferrous AMD stream is split into two. One stream is oxidized to ferric and the streams are then recombined at an elevated pH whereupon magnetite is formed. Wang, W. et al, 'Fundamental Study of an Ambient Temperature Ferrite Process in the Treatment of Acid Mine Drainage', Environ. Sci. Technol. 1996, 30, 2604-2608 found the optimum ferric:ferrous ratio for ambient temperature magnetite formation to resemble the stoichiometric ratio (i.e. 2:1) of these ions in magnetite. These authors also investigated the effects of both non-ferrous metals (as found in a Canadian AMD) and calcium on ambient temperature ferrite formation. Finding that calcium, but not non-ferrous metals, interfered decisively with ferrite formation, this same group investigated the effects of magnetite seed. It was found that magnetite seed restored the capacity for ferrite formation at ambient temperature in the presence of calcium: and a 'seeded ambient temperature ferrite process' for AMD was presented. This scheme requires stoichiometric adjustment by supplementary ferrous salt addition, as described in McKinnon W. et al, "Magnetic Seed in Ambient Temperature Ferrite Process Applied in Acid Mine Drainage Treatment", Environ. Sci. Technol. 2000, 34, 2576-2581. Earlier, Perez, O.P. et al, 'Precipitation and densification of magnetic iron compounds from aqueous solution at room temperature', Hydrometallurgy 50 (1998) 223-242 found that recycling of magnetic precipitates formed during (i.e. a one-step process) the oxidation of ferrous sulphate solutions in the presence of calcium had a positive effect on ferrite formation at ambient temperature.

The invention will now be described in more detail with reference to the following examples in which various aspects of the process according to the invention were investigated experimentally, and with reference to the accompanying drawings in which

FIGURES 1(a) and (b) show, in respect of Example 1, Mössbauer spectra at pH=10.5 and a seed concentration=4.8g/ℓ, at air flow rates of 0.12 ℓ/min (Figure 1(a)) and 0.6 ℓ/min (Figure 1(b)); in each case, the heavy solid line representing the theoretical fit of the two sub-spectra indicated by lighter lines;

FIGURE 2 shows, in respect of Example 1, sludge stability at pH=2 and pH=5;

FIGURE 3 shows, in flow diagram form and in respect of Example 3, the reactor system used to establish the steady-state ferrous intermediate concentration threshold for magnetite formation in the absence of calcium; both reactors are mixed continuously;

FIGURE 4 shows, in respect of Example 3, data for the ferrous intermediate concentration under steady-state operation, with the dark points being the values for the first reactor and the light points being the values for the second reactor;

FIGURE 5 shows, in respect of Example 3, an XRD trace for the precipitate formed at a ferrous intermediate concentration of about 100mg/ℓ; residual magnetite seed was first dissolved in concentrated HCl and filtered off;

FIGURE 6 shows, in flow diagram form and in respect of Example 4, the reactor system used to investigate magnetite formation in the presence of calcium; both reactors are mixed continually;

FIGURE 7 shows, in respect of Example 4, the ferrous intermediate concentrations maintained in the oxidation reactors for two experiments conducted in the presence of calcium; it is evident that the ferrous intermediate concentration is very stable and easily controlled;

FIGURE 8 shows, in respect of Example 4, that the seed concentration in the oxidizing reactor is easily controlled; and

FIGURES 9(a) and 9(b) show, in respect of Example 4, an XRD trace (Figure 9a) and a MS trace (Figure 9b) for sludge from experiments conducted in the presence of calcium (ferrous intermediate concentration of 1200-1700mg Fe/ℓ); the result shows the presence of magnetite with no other significant peaks appearing.

EXAMPLE 1

Batch processes according to the invention were investigated as regards the effects of pH, temperature, air flow rate and seed concentration on magnetite formation under batch conditions.

Materials and Methods

Reagents

The following analytical reagents (Sigma-Aldrich) were used as received: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Na_2SO_4 , NaOH , KOH , hydrazine sulphate, KNO_3 , NaHCO_3 , 32% HCl , 1,10-phenanthroline monohydrate, glacial acetic acid, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

Instrumentation and method for measurements

PH was measured with a Metrohm pH probe-temperature transducer coupled to a Metrohm 744 meter. Dissolved oxygen was measured with a USI5739 DO probe coupled to a Hitec Micro Systems (Cape Town, SA) meter. Bottled air and nitrogen, fed through rigid gas tubing, were passed sequentially via an adjustable pressure regulator and a rotameter flow meter to the reactor. At the reactor, soft flexible tubing conveyed the gases to a diffuser fixed to the middle of the reactor floor. Ferrous iron was measured by the phenanthroline method (Standard Methods, 1998). Total iron was determined by atomic absorption using a Varian SpectrAA 30 spectrometer. During a cycle, total iron was measured using a bench-top Spectroquant (Merck) system. Magnetite which served as the initial seed to start up each experiment was made according to the method suggested by Regazzoni et al (1981).

All batch experiments were performed in a clear Perspex reactor with internal dimensions of $18.75 \times 11.5 \times 11.5 \text{ cm}^3$ (height x width x width) capable of holding 2.62 ℓ . The reactor was fitted with a lid which had a large centrally-positioned circular port and four smaller ports positioned in each corner. The central port accommodated the shaft of the mixed paddle ($7.5 \times 2.5 \text{ cm}^2$, width x height) which rotated through a bearing fixed above the reactor. The top of the paddle was located 7cm above the reactor floor and was centrally positioned directly above the bubbler through which air/ N_2 are released. The large central port was also used to add reagents to and take samples from the reactor and also accommodated the DO probe.

Experimental procedure

Each experiment consisted of a sequence of repeated batch cycles. The procedure for each cycle was identical: the premix consists of distilled water containing from 1.2 to 8.4g/ℓ of seed, as required, which was stirred continuously at 187r/min. Prior to the addition of ferrous sulphate, N₂ gas was liberally bubbled for 10 minutes from the bottom of the reactor in order to deoxygenate the premix which was maintained at a pH below 4 at this stage. 0.0215M/ℓ of FeSO₄·7H₂O (giving an initial ferrous concentration of 1200mg/ℓ) was then added to the reactor. This established the desired seed: ferrous (Fe:Fe) ratio, e.g. a seed: ferrous (Fe:Fe) starting ratio of 7:1 when the seed concentration was 8.4g/ℓ. NaSO₄ was then added to establish a SO₄²⁻:Fe ratio of 2:1 characteristic of AMD. The pH was then raised to 10.5 by the addition of 5m NaOH and aeration commenced at 0.05 ℓ/min (air pressure upstream of the flow meter=100kPa). 1m ℓ samples were then taken at regular intervals until the end of the cycle. During the course of the cycle the pH was maintained at 10.5 by the addition of small volumes of 1M NaOH. The amount and time of addition of each dose of NaOH was recorded. Changes in the DO value were also recorded. Prior to the commencement of the next cycle a calculated amount of seed was removed from the reactor in order to restore the seed concentration to 8.4g/ℓ. The supernatant was also removed and replaced twice with distilled water between cycles in order to prevent salinity accumulating in the reactor.

Experiments without seed

These were conducted in an identical fashion to that described above, the only differences being that no seed was present in the premix and no recycling was performed.

Sludge settling tests

At the end of the cycle, mixing was stopped and the suspended solids were allowed to settle. After 30 minutes of settling time the volume of the settled solids was measured. Settlement results are depicted as sludge volume index (SVI) (Standard Methods, 1998).

Supernatant measurements

2 hours after the end of the cycle a 5mℓ sample of raw supernatant was taken, and without further processing, assayed for total iron concentration.

Sampling procedure during cycle

The 1mℓ samples taken during each cycle were taken from approximately halfway down the depth of the reactor. Each 1mℓ sample of reactor contents was immediately diluted to 100mℓ in a volumetric flask with 0.01M HCl (pH2). The sample was mixed by shaking and was allowed to stand for 5 minutes. The sample was then vacuum filtered through a 0.45 micron membrane filter and 50mℓ of the filtrate were set aside for later analysis of total iron and ferrous iron concentrations. The remaining filtrate was used to monitor total iron concentration during the course of a cycle. The membrane filter used to process the final sample for any cycle was retained and allowed to dry at room temperature overnight. The residue of seed and precipitated solids on the filter was then subjected to XRD and MS analysis.

Results

Figures 1a and 1b shows the mossbauer spectra of the final precipitate made under batch conditions using 2 different air flow rates using a pH=10.5 and seed concentration=4.8g/ℓ. Figure 1a had an air flow rate of 0.12ℓ/min while the air flow rate for Figure 1b was 0.6ℓ/min. Both spectra are typical of magnetite, although at 0.6ℓ/min there is a marked decrease in the % ferrous (i.e. charge compensating vacancies) evident as spectral line broadening and collapsed magnetic fields seen at the centre of the spectrum. This result proves that no, or little (undetectable) amounts of other (non-magnetite) iron oxides are formed. X-ray diffraction (xrd), transmission electron microscopy and chemical analysis all confirmed this finding (data not shown).

Stoichiometric magnetite has a % ferrous of 33,33%. Under batch conditions, the % ferrous varied between 32 and 17% (i.e. partially oxidised magnetite). Tables 1-3 show these variations as a function of air flow rate (intensity of oxidation), seed

concentration, pH and temperature. In all cases, the precipitate consists purely of magnetite, albeit magnetite of varying stoichiometry. In other words, the resulting magnetite is partially oxidized to a degree dependent on the seed concentration, air flow rate, temperature and pH.

TABLE 1

Effect of initial seed concentration and airflow rate on the ferrous to total iron ratio (shown in %) in the sludge. Results are given as average \pm standard deviation.

Initial seed concentration (g Fe/ ℓ) (initial seed to Fe ²⁺ ratio)	Air flow rate (ℓ /min)			
	0.05	0.085	0.12	0.6
0	5.7	-	-	-
1.2 (1 to 1)	32.15 \pm 0.42	28.86 \pm 0.24	27.42 \pm 1.70	17.36 \pm 0.74
4.8 (4 to 1)	32.03 \pm 0.72	30.86 \pm 0.01	29.61 \pm 0.73	21.49 \pm 1.59
8.4 (6 to 1)	30.52 \pm 0.51	-	-	27.60 \pm 1.54

TABLE 2

% ferrous results for pH=9 compared to those for pH=10.5 at a seed concentration of 4.8g.

Air flow (ℓ /min)	% ferrous	
	pH=9	pH=10.5
0.05	27.7	32.03
0.085	25.77	30.86
0.12	21.34	29.61

TABLE 3

Effect of temperature on % ferrous in the end-product (airflow rate = 0.085 ℓ /min, seed concentration = 4.8 g/ ℓ).

Temperature (°C)	23 ± 1	13 ± 1	7 ± 2
% ferrous to total iron	30.86 ± 0.01	24.24 ± 1.77	19.04 ± 0.01

Figure 2 shows the results of sludge stability studies (leaching tests). It is seen that at pH=5 the sludge is completely stable, whilst at pH=2 some slow weight loss does occur (stability at pH=5 is much more important than at pH=2 where it is still good).

Table 4 shows the sludge volume index (SVI) as a function of air flow rate and seed concentration (i.e. it settles well which is important.)

TABLE 4

SVI in ml/g according to seed concentration and airflow rate.

Seed concentration (g/l)	Air flow rate (l/min)			
	0.05	0.085	0.12	0.6
1.2	11.39	32.56	32.19	67.61
4.8	7.38	14.41	22.02	28.47
9.6	8.00			16.04

EXAMPLE 2

This example shows the effect of calcium in the water. Under batch conditions calcium, present in equimolar concentrations with respect to ferrous, inhibits magnetite formation. At 0.12 l/min air flow rate and a seed concentration of 4.8g/l, % ferrous in the sludge was only ~13%. The corresponding value in the absence of calcium was 29.61%. Increasing the seed concentration to 8.4g/l had the effect of increasing the % ferrous to 18.8%. Maximum purity under batch conditions is therefore less than 60% (as stoichiometric magnetite). Macroscopic inspection (brown colour, instead of black), XRD and mossbauer analysis all indicated the presence of significant quantities of non-magnetite phases (which may be undesirable).

EXAMPLE 3

This example investigated steady-state conditions.

From a process perspective, ambient temperature magnetite formation was investigated in a completely mixed continuous reactor which allows the attainment of steady-state conditions, particularly as regards seed and ferrous intermediate concentrations.

The initial configuration used for a steady-state process is depicted in Figure 3 which shows the reactor system or process used to establish the steady-state ferrous intermediate concentration threshold for magnetite formation in the absence of calcium.

Thus, in Figure 3, reference numeral 10 generally indicates the experimental apparatus used to simulate the process of the invention. The apparatus 10 includes a 5.2ℓ oxidation reactor 12, with an air line 14 (for aeration purposes) and a raw AMD influent (Fe^{2+}) line 16 leading into the reactor 12. A transfer line 18 leads from the reactor 12 to a gravity settler 20. An effluent line 22 leads from the settler 20, as does a sludge or slurry line 24. The line 24 thus leads from the bottom of the settler 20. The line 24 leads to a second 2.5ℓ oxidation reactor 26. An air line 28, for aeration purposes, leads into the reactor 26, while a sludge disposal line 30 leads away from the reactor 26. A recycle line 32 leads to the reactor 12. The pH of the water in the reactors 12, 26 was maintained or controlled at 10.5 by means of NaOH addition (not shown).

It was found that a ferrous intermediate concentration threshold in the oxidising reactor 12 critically governs the end product. Both reactors 12, 26 were mixed continually. Figure 4 shows the concentration of ferrous intermediate in the two oxidising reactors 12, 26 for the case where the target concentration was 500mg/ℓ. Above ~500mg/ℓ ferrous intermediate (as ferrous), magnetite is formed. Below ~500mg/ℓ ferrous intermediate, the non-ferrite goethite begins to form in detectable amounts (which is bad). As the steady-state ferrous intermediate concentration decreases, goethite becomes the major iron oxide formed (Figure 5). The % ferrous of the magnetite formed with a ferrous intermediate concentration of ~500mg/ℓ was 28%.

In the light of this finding, it is clear that batch tests are not homogeneous with respect to a critical parameter, and that a steady-state process is highly advantageous, since the ferrous intermediate concentration can be maintained above $500\text{mg}/\ell$, thus ensuring pure magnetite formation. Steady-state reactors are also smaller and consequently less expensive to construct.

As shown in Figure 3, a second oxidizing reactor 26 was introduced into the thickening-recycle limb. That is, the effluent from the first oxidising reactor 12, which has a ferrous intermediate concentration of $\sim 500\text{mg}/\ell$, is passed to a settling tank 20. Here, the "seed-ferrous intermediate complex" is concentrated around 3 - 5 times or more. The underflow from the settler can then be pumped to the second smaller reactor 26 and oxidized by aeration down to a ferrous intermediate concentration of $\sim 500\text{mg}/\ell$ (or lower) again. In this way, ferrous can, importantly, be exhaustively converted to magnetite prior to sludge disposal.

EXAMPLE 4

This example investigates the effect of calcium in steady-state operation.

The process configuration used is depicted in Figure 6.

Thus, in Figure 6, reference numeral 100 generally indicates the experimental apparatus used to simulate the process of the invention. The apparatus 100 included a 2.5ℓ precipitation (contact) reactor 102, with an AMD influent ($\text{Fe}^{2+} + \text{Ca}^{2+}$ i.e. simulating the use of lime) line 104 leading into the reactor 102. A line 106 leads by gravitational flow from the reactor 102 to a gravity settler 108. A sludge withdrawal line 110 leads from the bottom of the settler 108. Waste sludge can be withdrawn from the settler 108 along the line 110 for sludge stabilization treatment. A sludge line 112 also leads from the bottom of the settler 108 to an oxidation reactor 114. An effluent withdrawal line 116 also leads from the settler 108. An air line 118, for aeration purposes, leads into the reactor 114. A seed recycle line 120 leads from the reactor 114 to the reactor 102. The pH in both reactors 102, 114 was maintained or controlled at 10.5 by means of NaOH addition (not shown).

The influent consisted of separate, equal volumes at equal flow rates, equimolar ferrous and calcium solutions (ferrous solution = 0.359M ferrous = 4g-Fe/ ℓ , sulphate concentration raised to twice that of the ferrous by the addition of sodium sulphate; calcium solution = 0.359M calcium chloride). The pH of the precipitation reactor 102 is maintained at 10.5 so that the "seed-ferrous intermediate complex" is formed instantly. Gravitational overflow carries the liquor to the settling tank 108 where thickening occurs. The concentration of ferrous intermediate is then maintained above 1200mg/ ℓ in the oxidising reactor 114. Sludge is wasted by means of the sludge withdrawal line 110 on a regular basis. Wasted sludge can be further concentrated in a settling tank (not shown) and then aerated until all ferrous is converted to stable end product. A recycle loop 120 takes seed back to the precipitation reactor 102.

In this proof-of-concept research, the reactor system was run under the following conditions:

- Volume_{oxidising reactor} = 5.2 ℓ , Volume_{precipitation reactor} = 2.5 ℓ .
- Ferrous load_{influent} = 3.6g-Fe/hour (= 60mg/min = ~11.5mg/L/min).
- [seed]_{oxidising reactor} = 18.21 \pm 1.52 g, [seed]_{precipitation reactor} = approx. 4 \pm 2 g.
- Air flow rate_{oxidising reactor} = 0.06 ℓ /min.
- Total seed mass = 92g, sludge age_{total system} = 25.5 hours.
- RT_{oxidising reactor} = 10.8 hours, RT_{precipitation reactor} = 1.2 hours. (RT_{seed} = RT_{hydraulic}).
- [ferrous intermediate]_{oxidising reactor} = 1522 \pm 223 mg.
- pH = 10.5 \pm 0.2, both reactors.
- Temperature = 22 \pm 2 $^{\circ}$ C.

It must be noted that the ferrous intermediate concentration is above 1200mg/ ℓ (Fig. 7, Experiment 2), well above the critical threshold value below which goethite is known to form in the absence of calcium. In the presence of calcium, a high ferrous intermediate concentration inhibits the calcium interference effect.

Under these conditions it was found that:

- Pure magnetite is formed despite the presence of calcium as shown by xrd (Figure 9a) and mossbauer spectroscopy (MS) (Figure 9b).
- High quality magnetite is formed (% ferrous ~ 30%).
- Ferrous iron is transformed into magnetite at a rate of $10.79 \pm 1.52 \text{ mg-Fe}/\ell/\text{min}$.
- The iron content in the final effluent is less than $1 \text{ mg}/\ell$ (>99.9% removal efficiency).
- The solids settle rapidly and completely (average $\text{SVI}_{\text{oxidising reactor}} = 3.17 \text{ m}\ell/\text{g}$).
- The very low SVI in the oxidising reactor means that waste sludge can be easily re-thickened and oxidised until all ferrous is exhausted.
- The critical parameters are easily controlled and extremely stable: air flow rate, [ferrous intermediate], [seed] and pH (Figure 7, experiment 2; Figure 8), where [] denotes concentration of the component given in the brackets.
- Gypsum precipitation: calculated concentrations of free calcium and sulphate ions in the precipitation reactor exceed the solubility product of gypsum, and crystals are indeed deposited on the walls of this reactor and in the settling tank. No crystal deposition was observed in the oxidising reactor however, indicating that the kinetics of precipitation are relatively rapid.

AMD waters typically contain concentrations of ferrous iron which are orders of magnitude higher than the concentrations of other metals. The ambient temperature ferrite process transforms the ferrous iron into the ferrite magnetite (Fe_3O_4). During its formation, magnetite has the capacity to absorb non-ferrous mono-, di-, tri- and tetravalent metal ions into its crystal lattice (cation substitution). In all of the above descriptions of the process, non-ferrous metals which may be present in the ferrous-containing water, may be incorporated as mixed species ferrites into the precipitate.

At high temperatures, the oxidation product of ferrous iron is the ferrite magnetite. The high temperature ferrite process is a proven technology but is unsuitable for large volumes such as AMD. At low temperatures, in the absence of magnetite seed, oxidation of ferrous iron produces a mixture of iron oxides. The processes of the invention address three key challenges in developing an ambient temperature ferrite process suitable for AMD treatment:

- (1) channelling the reaction towards ferrite formation at ambient temperature,

- (2) effecting viable reaction and settling rates, and
- (3) overcoming the interference of calcium when lime is used as a source of base (large diameter calcium ions appear to disrupt the crystal lattice and inhibit magnetite formation).

The invention thus proves that magnetite seed can be used to channel the reaction towards magnetite formation at ambient temperature. The invention also solves the calcium interference effect as well. Excellent sludge settling properties, the formation of an environmentally stable sludge, and short retention times for the bulk AMD volume or other wastewater being treated, are further advantages.

CLAIMS:

1. A process for treating water, which includes
adding magnetite seed to water containing dissolved ferrous and/or non-ferrous metals, to form seeded water;
if necessary, adding ferrous iron to the water;
if necessary, raising the pH of the seeded water to a level at which a solid ferrous intermediate forms, or is present, in the seeded water and/or maintaining the water at such a pH level;
subjecting the resultant seeded ferrous intermediate-containing water to controlled oxidation of the ferrous intermediate at substantially ambient temperature to produce, as an oxidation product, ferrite(s) comprising magnetite;
maintaining at least a predetermined or threshold ferrous intermediate concentration in the water during the controlled oxidation of the water; and
separating the ferrite from the water.
2. A process according to Claim 1, wherein the pH to which the seeded water is raised and/or at which it is maintained, is at least 9.0.
3. A process according to claim 2, wherein the pH to which the seeded water is raised and/or at which it is maintained is about 10.5.
4. A process according to any one of claims 1 to 3 inclusive, wherein the controlled oxidation is effected by aerating the seeded ferrous intermediate-containing water.
5. A process according to Claim 4, wherein the rate at which the seeded ferrous intermediate-containing water is aerated is controlled so that the ferrous intermediate oxidizes primarily to ferrite(s) consisting mainly of magnetite, with substantially no non-ferrite compounds forming.
6. A process according to any one of Claims 1 to 5 inclusive, wherein sufficient magnetite seed is added to the ferrous-containing water so that the molar ratio of the initial seed (as Fe):ferrous intermediate (as Fe) is at least 1:1.

7. A process according to any one of Claims 1 to 6 inclusive, which operates in a steady state continuous manner.
8. A process according to Claim 7, which includes a contact-separation sequence in which raw water containing dissolved ferrous and/or non-ferrous metals is mixed or contacted with water containing magnetite seed and ferrous intermediate at an elevated pH of at least 9.0, whereafter solid components present in the resultant water mixture are partially separated, as a slurry or suspension, from the water phase, with the slurry or suspension then being subjected to the controlled oxidation.
9. A process according to Claim 8, wherein the mixing or contacting of the raw water with the water containing the magnetite seed and ferrous intermediate is effected at a pH of about 10.5.
10. A process according to any one of Claims 7 to 9 inclusive, wherein the predetermined or threshold ferrous intermediate concentration in the water is controlled so that the ferrous intermediate, during the controlled oxidation, oxidizes primarily to ferrite(s) consisting mainly of magnetite, with substantially no non-ferrite compounds forming.
11. A process according to Claim 10, wherein the predetermined or threshold ferrous intermediate concentration in the water is about 500mg/ℓ.
12. A process according to any one of Claims 7 to 11 inclusive, wherein the ferrous-containing water contains also calcium, with the magnetite seed concentration then being maintained at a higher level than when the ferrous-containing water does not contain calcium, in order to counter the inhibitory effect which calcium has on ferrite formation.
13. A process according to Claim 12, wherein the predetermined or threshold ferrous intermediate concentration in the water is about 1200mg/ℓ.
14. A process according to Claim 12 or Claim 13, wherein the seeded ferrous intermediate containing water is saturated or slightly supersaturated with dissolved

calcium, with the predetermined or threshold ferrous intermediate concentration in the water being at least 1500mg/ℓ.

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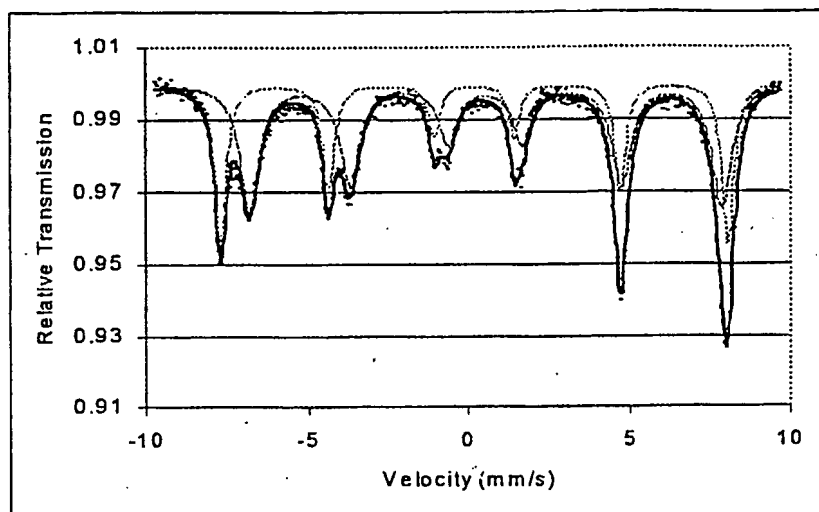


FIG 1a

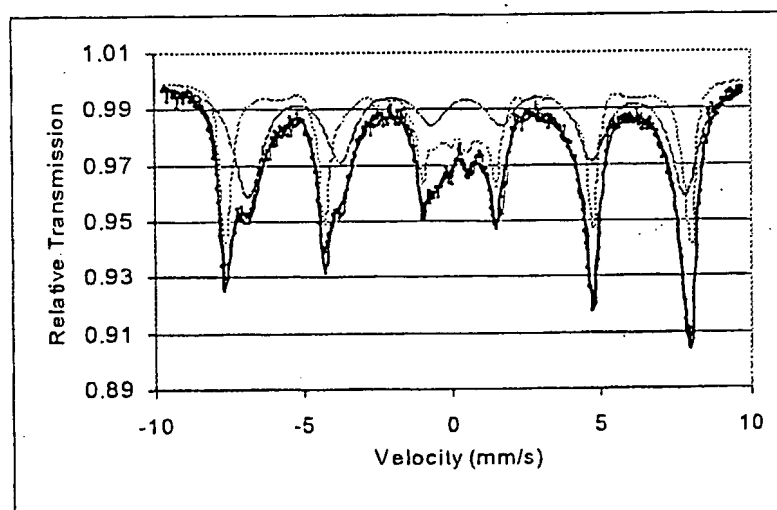


FIG 1b

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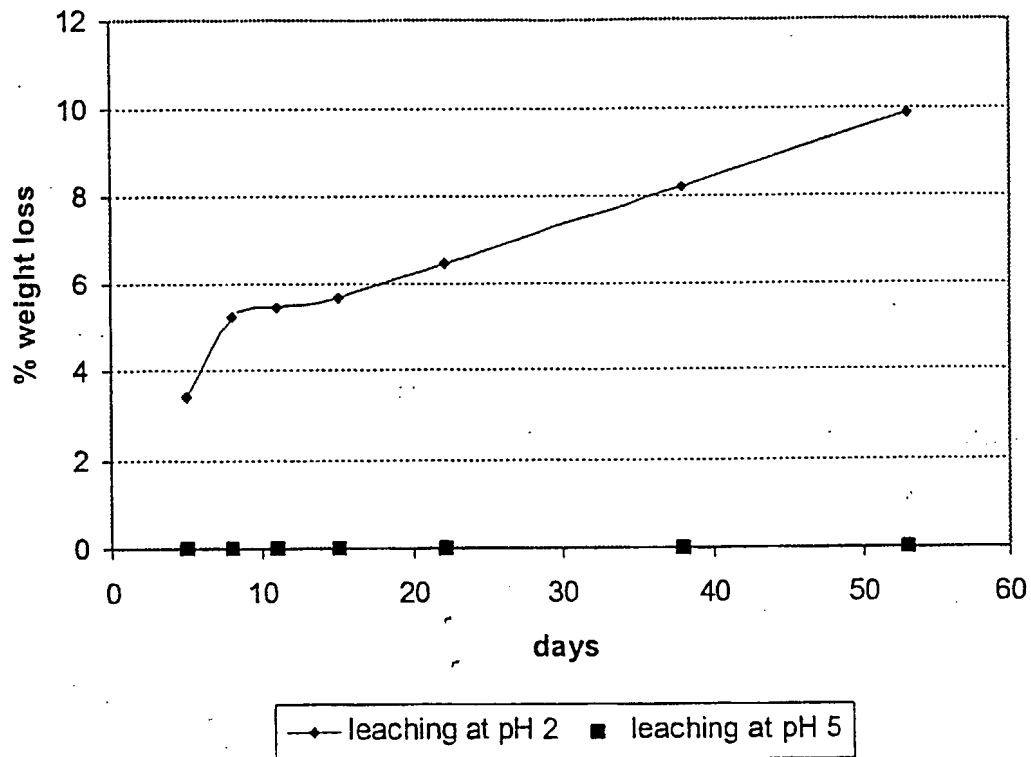


FIG 2

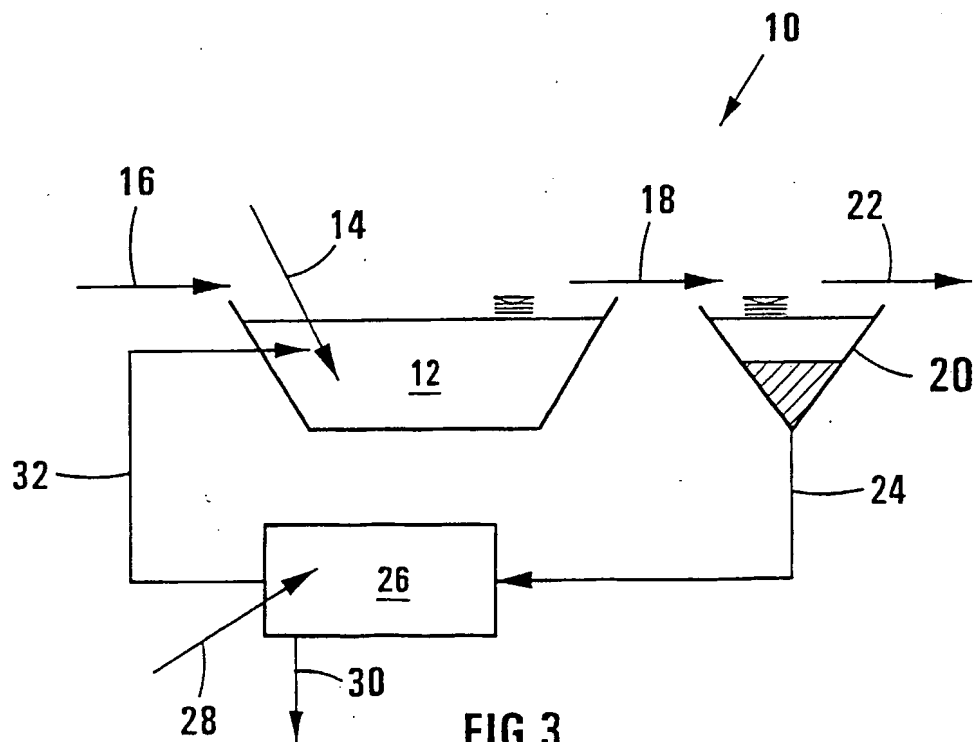
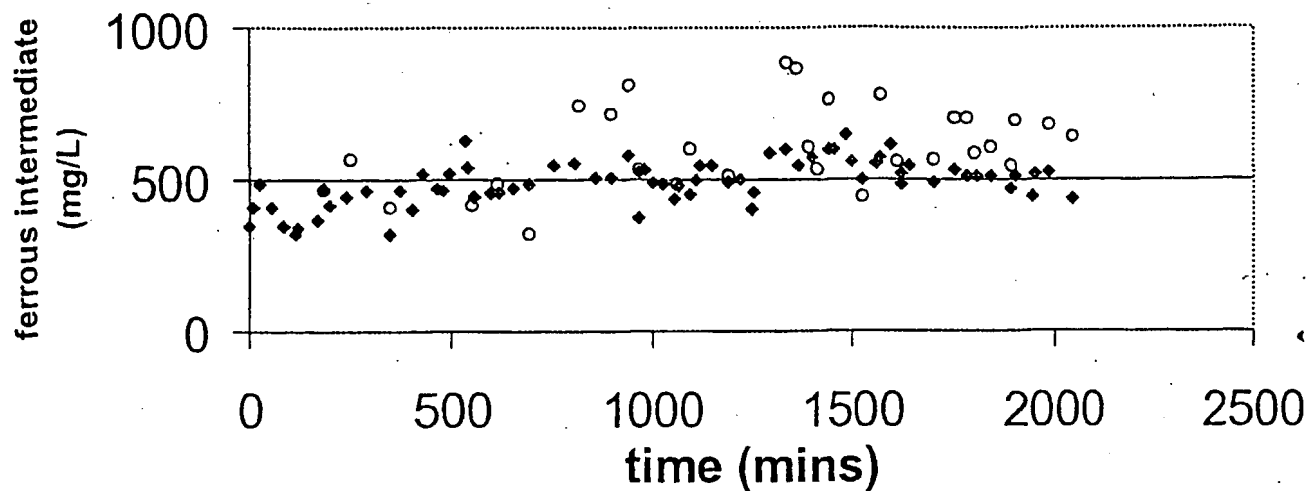
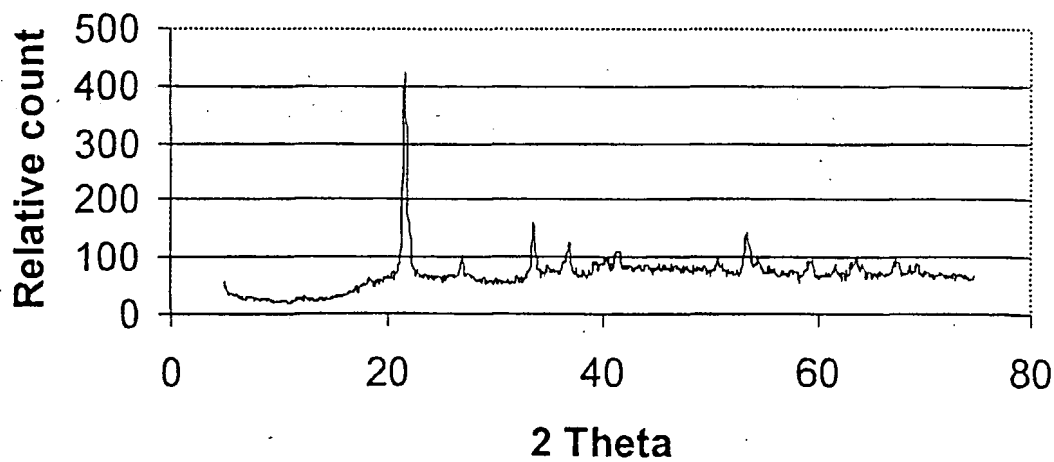


FIG 3

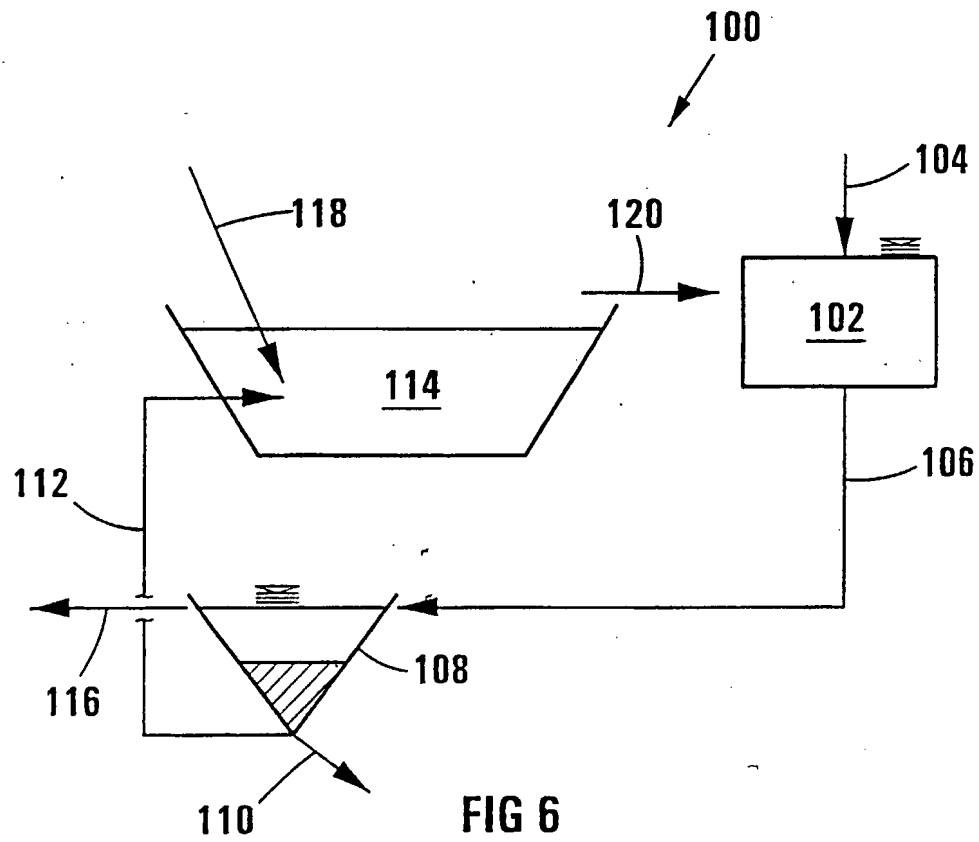
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Steady-state: ~500mg/L**FIG 4****Steady-state: ~100mg/L
(after conc. HCl)**

— Goethite

FIG 5

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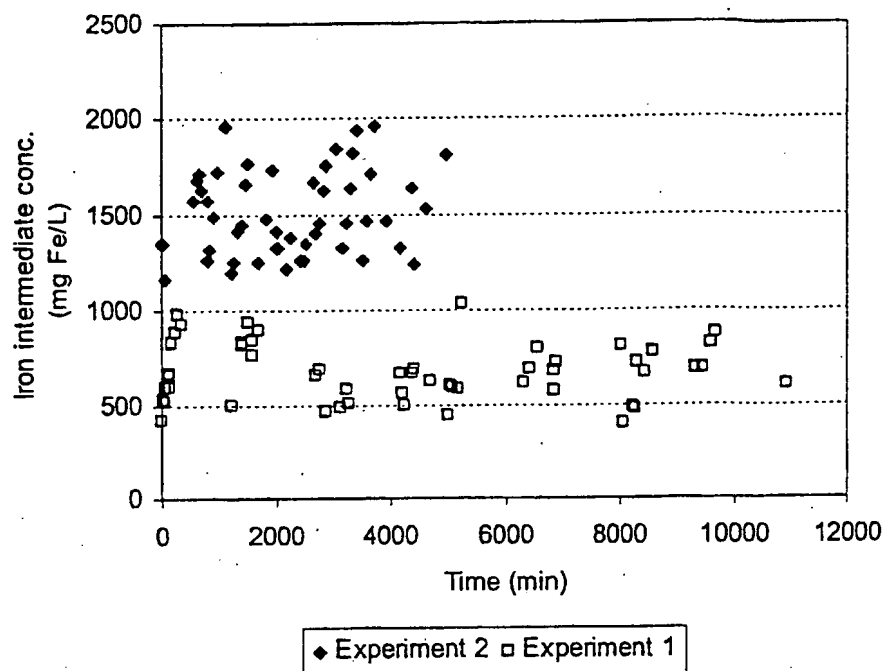


FIG 7

Seed concentration in oxidising reactor

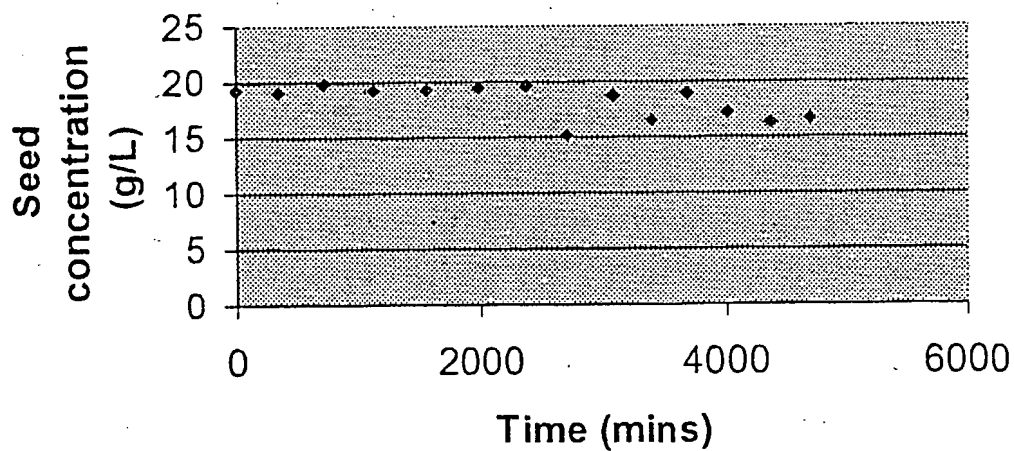


FIG 8

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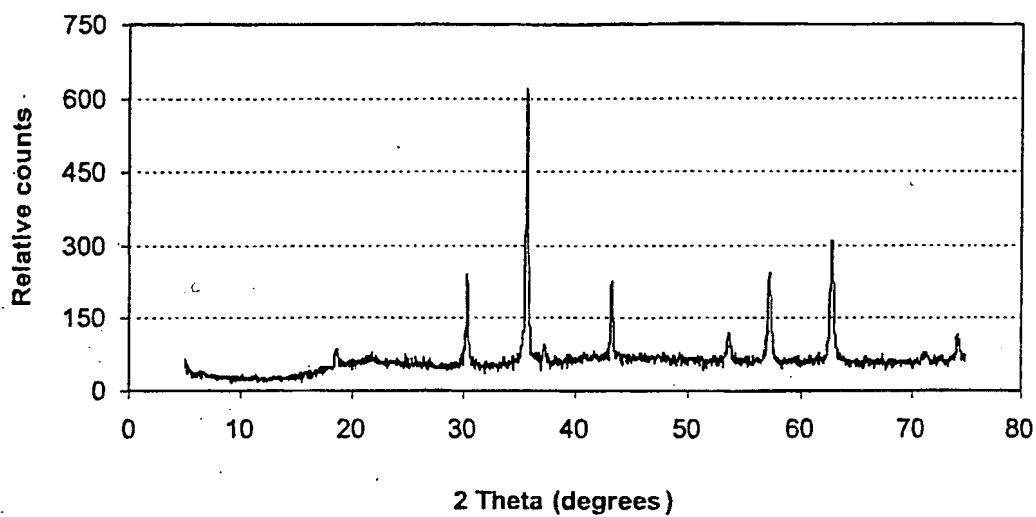


FIG 9(a)

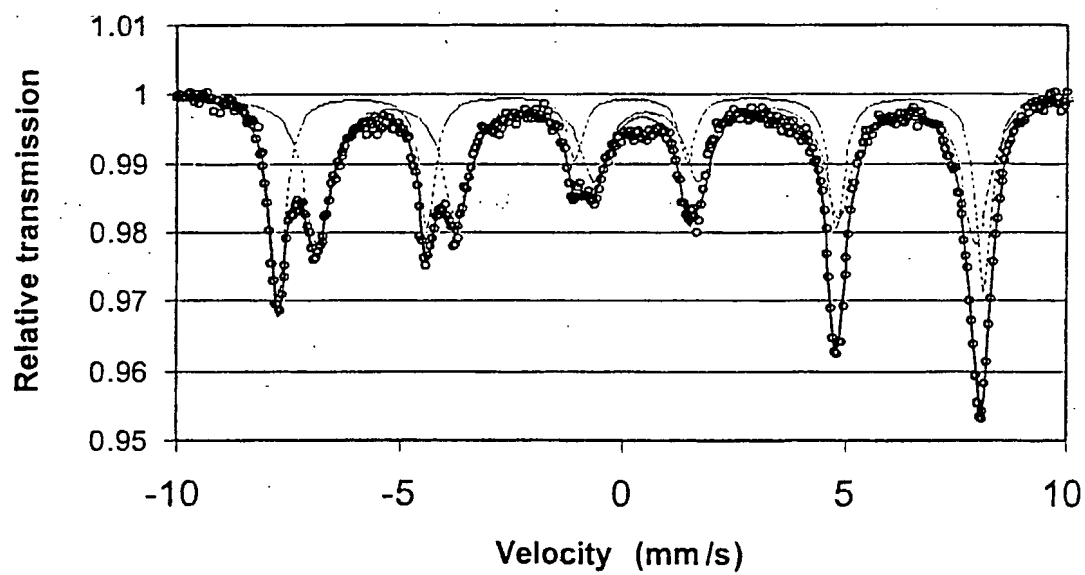


FIG 9(b)

INTERNATIONAL SEARCH REPORT

PCT/IB 03/01875

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/74 C02F1/52 C02F1/64 C02F1/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, BIOSIS, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MORGAN B E ET AL: "Fundamental study of a one-step ambient temperature ferrite process for treatment of acid mine drainage waters"	1-11
Y	WATER SA; WATER SA 2001, vol. 27, no. 2, 2001, pages 277-282, XP002252377 the whole document --- -/--	12-14

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 August 2003

Date of mailing of the international search report

12/09/2003

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Glod, G

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MCKINNON W ET AL: "Magnetic seed in ambient temperature ferrite process applied to acid mine drainage treatment" ENVIRON SCI TECHNOL; ENVIRONMENTAL SCIENCE AND TECHNOLOGY 2000 ACS, WASHINGTON, DC, USA, vol. 34, no. 12, 2000, pages 2576-2581, XP002252378 cited in the application	1,4-7
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P, X	--- MORGAN B E ET AL: "A seeded ambient temperature ferrite process for treatment of AMD waters: Magnetite formation in the presence and absence of calcium ions under steady state operation" WATER SA; WATER SA APRIL 2003, vol. 29, no. 2, April 2003 (2003-04), pages 117-124, XP002252380 the whole document	1-14
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